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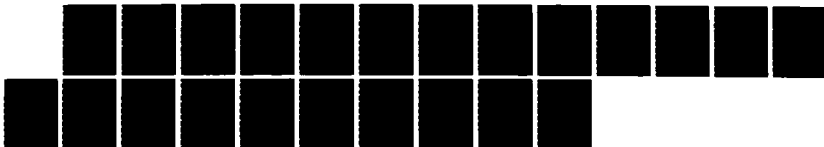
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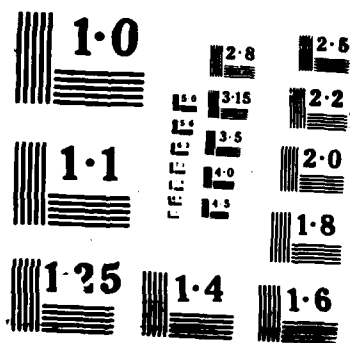
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The Dependence of the Reaction Probability of Benzene on the Size of Gaseous Niobium Clusters

by

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DEPENDENCE OF THE REACTION PROBABILITY OF
BENZENE ON THE SIZE OF GASEOUS NIOBIUM CLUSTERS

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ABSTRACT

Small niobium atomic clusters (Nb_x , $x = 1-15$), synthesized by laser vaporization in a supersonic molecular beam system, are mixed with benzene in a fast flow reactor and detected by excimer laser photoionization time-of-flight mass spectrometry. The ratio of the observed mass peak ion intensity of Nb_xC_6 to that of $Nb_xC_6H_6 + Nb_xC_6H_5$ at low excimer laser intensities is used as a measure of the observed conversion of $Nb_xC_6H_6$ into Nb_xC_6 . This probability is found to have a threshold for conversion near $x = 4$ with maxima at $x = 5$ or 6 and 11 . The ratio also shows a minimum for those clusters containing 8 and 10 atoms, similar to the previously observed reactivity of these two clusters and their cations toward H_2 and N_2 . This observed variation in the $Nb_xC_6H_6$ to Nb_xC_6 conversion reaction is discussed in terms of the stabilities of benzene and the bare metal clusters relative to Nb_xC_6 and $3H_2$.

INTRODUCTION

The laser technique¹ for synthesizing cold, isolated clusters of practically any element or alloy has introduced exciting opportunities for investigating the fundamental chemical and physical properties of transition metal clusters. This method, which incorporates laser vaporization of a solid target within a pulsed helium beam, generates isolated clusters consisting of $2-10^2$ atoms with densities high enough for spectroscopic and mass analysis.^{2,3} This makes it possible to do a variety of studies on the physical and chemical properties of these unique species.

Several studies thus far have used the advantages of cluster synthesis in molecular beams to examine the electronic and magnetic properties through measurements of their ionization potentials³ and magnetic moments.⁴ The chemistry of clusters has also been examined through experiments on their relative reactivity and kinetics in a fast flow reactor.^{5,6} The present work adds to these latter studies in an effort to understand the simple chemical behavior of transition metal clusters.

In this work, laser mass spectrometry techniques are used to study the reaction between niobium clusters Nb_x , with $x = 1-15$, and benzene. We focus only on the formation of $Nb_xC_6H_6$ and Nb_xC_6 , since they are among the most intense reaction product mass peaks. We have used the ratio of the mass peak intensities of Nb_xC_6 to the sum of $Nb_xC_6H_6 + Nb_xC_6$ as a measure of the reaction probability of benzene with the Nb_x clusters. The dependence of this probability on the cluster size is obtained and discussed in terms of the relative reactivity of the different clusters.

EXPERIMENTAL

Niobium metal clusters are generated by Nd:YAG laser vaporization of a rotating solid niobium rod in the midst of a helium molecular beam pulse similar to that previously described by Smalley et al.⁷ The metal atom plume formed from the rod is entrained and quenched in the helium pulse where condensation/nucleation results in cluster formation. The clusters are then expanded into our fast flow reactor tube where a pulse of reactant gas mixture overlaps with the metal cluster beam. The reactant is pulsed into the stream of clusters such that the overlap and mixing with the metals is maximized. The average density in the reaction region is calculated to be ~200 torr with a 0.1 to 0.2% reactant concentration in helium. The retention time of the metal clusters in the reactor is measured to be ~120 μ s with an estimated reaction temperature of 300-400 K. The cluster mixture is then expanded into a high vacuum system where a sudden decrease in temperature and density stops further reactions from occurring.

The cluster expansion passes through a 2-mm skimmer to form a well-collimated molecular beam with a total flight distance of 35 cm. Detection of the niobium clusters and their reaction products is done in a time-of-flight mass spectrometer with an ArF excimer laser as the ionizing source. In this study, the incident laser energy is kept in the 10 to 50 μ J per pulse range. An unfocused beam is used through a 2-mm aperture to assure that only single photon ionization occurs and thereby minimize multiphoton fragmentation of the reaction products. The laser intensity dependence of the mass peaks suggests the absence of multiphoton processes at this intensity. At higher laser intensities, evidence for photochemical changes are observed. These results will be discussed in a later publication.⁸ The photoions are then accelerated and analyzed by a 1.7-m TOF mass

spectrometer and collected on a multichannel plate ion detector. The signal is amplified, digitized, and stored as a mass spectrum on a VAX 11-780 computer.

The appearance of new product peaks from the addition of the reactant mixture is monitored by alternately using a control reactant which consists of only pure helium kept at the same pressure as the helium/reactant mixture. This allows for a comparison between the bare niobium cluster distribution and the new distribution formed when the reactant species are introduced into the reactor.

RESULTS AND DISCUSSION

Figure 1 shows the laser produced mass spectra of the niobium control cluster distribution and the niobium mixed with benzene distribution obtained in our fast flow reactor. These were obtained under identical conditions except that, in the latter spectrum, the helium gas introduced in the reaction zone contained 1.4% benzene vapor.

The upper spectrum (Figure 1a) shows the control distribution of Nb_1 through Nb_{15} taken with only pure helium being mixed into the reaction tube. The observed cluster distribution is centered around Nb_7 as the most intense peak by setting the appropriate deflection voltages on the TOF mass spectrometer. A peak for Nb_1 is not seen due to its ionization potential (6.8 eV) being higher than the 6.4 eV energy of the ionizing ArF laser photons. Satellite peaks to larger mass of the different Nb_x clusters are the Nb_xO_y oxide peaks from the reaction of oxygen with the metal clusters in the cluster formation region.

Figure 1b is the mass spectrum of the niobium clusters after being mixed with a 1.4% benzene in helium reactant mixture in the cluster reactor.

A number of new product peaks are observed. In the lower mass region from Nb_1 to Nb_3 , there are new peaks corresponding to $Nb_x(C_6H_6)_y$ masses with the peaks at $Nb_1(C_6H_6)_2$ and $Nb_2(C_6H_6)_2$ being the strongest product peaks detected. No sign of dehydrogenation of the benzene molecule is found in this region. For niobium clusters larger than Nb_3 , peaks corresponding to $Nb_xC_6H_6$ as well as Nb_xC_6 are found. In this region, the amount of dehydrogenation varies as a function of the parent Nb_x cluster size.

Figure 2 gives an expanded version of the reaction product mass spectrum in the Nb_4 to Nb_{11} range. Marked on the figure are the mass peaks for the $Nb_xC_6H_6$ and Nb_xC_6 in this region. Here Nb_6C_6 shows the strongest mass peak intensity relative to its corresponding $Nb_6C_6H_6$ mass peak. A similar behavior is observed for Nb_5 and Nb_{11} as well. Doublet peaks for the masses of both $Nb_7C_6H_6$, Nb_7C_6 and $Nb_9C_6H_6$, Nb_9C_6 clusters are clearly shown. However, inspection of the Nb_8 and Nb_{10} peaks reveals an absence of the totally dehydrogenated Nb_8C_6 and $Nb_{10}C_6$ species with the mass peaks for $Nb_8C_6H_6$ and $Nb_{10}C_6H_6$ being more intense.

Reaction of the Nb_xO_y clusters goes essentially unnoticed in the benzene reaction spectrum. Only in the region from Nb_4 to larger clusters do we see small oxide species become apparent. The lack of Nb_xO_y -hydrocarbon species indicates that they are either not detected or simply not produced. The presence of the oxide on the Nb_xO_y clusters may act as a protection group and stabilize the cluster, rendering it unreactive. We further noticed that the spectra show no resolved $Nb_x-C_yH_z$ progressions on the clusters with y or $z < 6$.

Is the chemistry we observe thermally induced or photochemically initiated by the ionizing laser? This is a very difficult question to answer. The possibility of multiphoton laser induced reactions is eliminated at the

laser intensities used (3 - 16 $\mu\text{J}/\text{mm}^2$) by carrying out the excimer laser intensity dependence of the Nb_xC_6 to $\text{Nb}_x\text{C}_6\text{H}_6$ mass peak intensity ratio.⁸ However, as in previous cluster reaction studies, one cannot easily distinguish between thermal reactions occurring prior to exposure to the excimer ionizing radiation and those induced during the one photon ionization process. In the latter case, product peak broadening can be observed unless the excess photon energy above ionization is sufficiently high to drive the reaction to completion in a time shorter than the acceleration time of the TOF mass spectrometer ($\sim 1 \mu\text{s}$). Our results show no characteristic peak broadening of reaction products indicating that any photo-induced reactions are occurring on a time scale shorter than microseconds. This can be the case if the adsorbed reagent greatly reduces the cluster ionization potential, and the decomposition reaction is highly exothermic.

The C_6H_6 observed on these clusters is most likely to be a chemisorbed benzene molecule and not $\text{C}_6 + 3\text{H}_2$. The fact that the small clusters give $\text{Nb}_x\text{C}_6\text{H}_6$ and the large clusters give Nb_xC_6 is consistent with this conclusion since the larger clusters would be expected to adsorb the 3H_2 more efficiently due to the increased surface area. Even more convincingly, Nb_8 and Nb_{10} have been shown not to bind readily to H_2 ,⁶ indicating that the C_6H_6 species on these clusters must be benzene.

The question now arises as to the nature of bonding in Nb_xC_6 . Is this a cluster of Nb_x and chemisorbed C_6 species made by the dehydrogenation of benzene? Could it be a chemical compound with strong NbC bonds? As usual, mass spectrometry alone cannot tell us the structure of these species. However, there are some facts that might suggest the involvement of the Nb-C chemical bonds. Niobium is known to form strong carbides of NbC composition. This together with the fact that the Nb_xC_6 species appears only

when $x \geq 4$ might suggest that, in these clusters, the formation of a large number of NbC bonds drives the chemical reaction and destroys the integrity of the stable benzene structure.

In an attempt to study the dependence of the probability of the conversion of benzene (C_6H_6) to C_6 on Nb_x clusters on the size of the cluster, we use the ratio of the intensity of the Nb_xC_6 peak to the sum of the peak intensities for both $Nb_xC_6H_6$ and Nb_xC_6 in the same spectrum. In principle, this ratio should be a more accurate monitor of the dependence of the reactivity of these clusters than the relative decrease in the bare Nb_x cluster mass peaks due to the reactions. This is because the distribution of the Nb_x clusters observed is sensitive to many parameters, e.g., the cluster formation conditions (the plasma characteristics), the reactor conditions, and the timing of the different components in the experiment (the cluster formation and reactant beam pulses, the vaporization laser pulse and the ionizing excimer laser pulse). Errors resulting from these experimental difficulties can be greatly reduced if mass peak intensity ratios of products from the same Nb_x cluster are used to follow the reactivity of those clusters. However, other sources of error remain or are introduced in the ratio method as discussed below.

In the low excimer laser intensity range, the observed mass peak ratio of two products formed on the same cluster Nb_x is given by:

$$\frac{I_{Nb_xP1}}{I_{Nb_xP2}} = \frac{I_1}{I_2} = \frac{C_1 \sigma_1 (1 - \beta_1) S_1}{C_2 \sigma_2 (1 - \beta_2) S_2}$$

where C , σ , β , and S are the concentration, the ionization cross section at the excimer laser frequency, the decomposition probability of the ion after its formation and the collection/detection efficiency of the ions formed,

respectively. Thus, only if the products formed on the same cluster have similar ionization, decomposition, and collection/detection efficiencies can the mass intensity ratios give a good determination of the concentration ratios of the products formed. If the ionization potentials of $\text{Nb}_x\text{C}_6\text{H}_6$ and Nb_xC_6 are not too different, we may assume that σ and σ' are comparable for the two products. Since the fractional difference in the mass of $\text{Nb}_x\text{C}_6\text{H}_6$ and Nb_xC_6 is small, the collection and sensitivity of detecting their corresponding ions can be assumed to be similar. Thus the ratio of the mass peak intensities can give a "rough" estimate of the concentration ratio. Furthermore, if one assumes that both C_6H_6 and C_6 reduce the ionization potential of the different clusters by not very different amounts as one changes the number of atoms in the cluster, variation in the mass peak ratio with the number of atoms (x) in the cluster can give a rough measure of the change in their reactivity.

A plot of the peak intensity ratio for Nb_xC_6 to the sum of the peak intensities for $\text{Nb}_x\text{C}_6\text{H}_6$ and Nb_xC_6 as a function of x (for $x = 1-15$) is given in figure 3. Here we can see that Nb_5 , Nb_6 , Nb_7 , Nb_9 and Nb_{11} are relatively active toward converting C_6H_6 to C_6 while Nb_8 and Nb_{10} are relatively inactive. The latter clusters⁶ and their cations⁹ are shown to be unreactive toward H_2 and N_2 as well. This observation suggests that since our method of measuring reactivity gives results consistent with other methods, the sources of errors discussed above do not wash out the relative chemical trends.

It is not known whether the observed reactive trends are kinetically or thermodynamically controlled. There are, however a number of the observations that can best be explained if one considers the relative stabilities of the reactants and the products:

1. The threshold for the size of cluster that converts benzene (C_6H_6) to C_6 could be explained by the need to make a large number of Nb-C bonds before the reaction that changes the relatively stable benzene ring can be thermodynamically feasible.

2. The observed maximum in the conversion probability at $x = 5-6$ and 11 could be attributed to these clusters having a maximum in the fraction of total bonds that are of the Nb-C type.

3. Neutral⁶ Nb_8 and Nb_{10} and their cations¹⁰ are found to be relatively unreactive toward H_2 and N_2 . As found in this work, these clusters are also unreactive toward benzene dehydrogenation. Since the mechanisms involved in the reactions with these molecules are expected to be different, it is possible that the low reactivity of the Nb_8 and Nb_{10} clusters is a result of their relatively high stability. This makes it difficult to drive any of the chemical reactions that would destroy the structure of these stable clusters. This stability might also explain the relatively high ionization potentials observed for these clusters.^{3e}

It is obvious that more experimental results are needed before a final conclusion regarding the different factors that determine the observed reactivities of these clusters can be drawn. Detailed ionization laser intensity and energy dependence studies of the product mass peaks are now in progress and the results will soon be published.⁸

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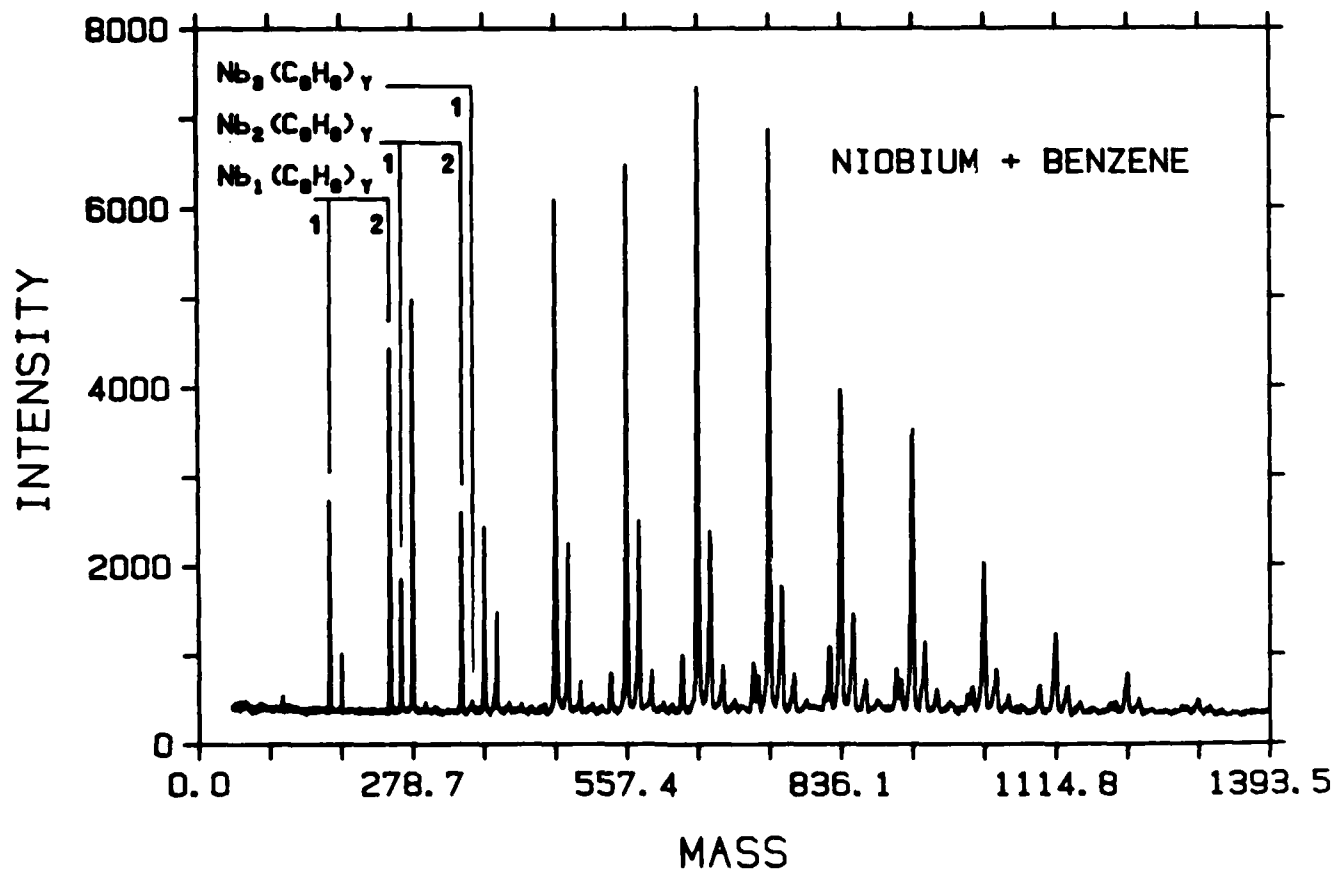
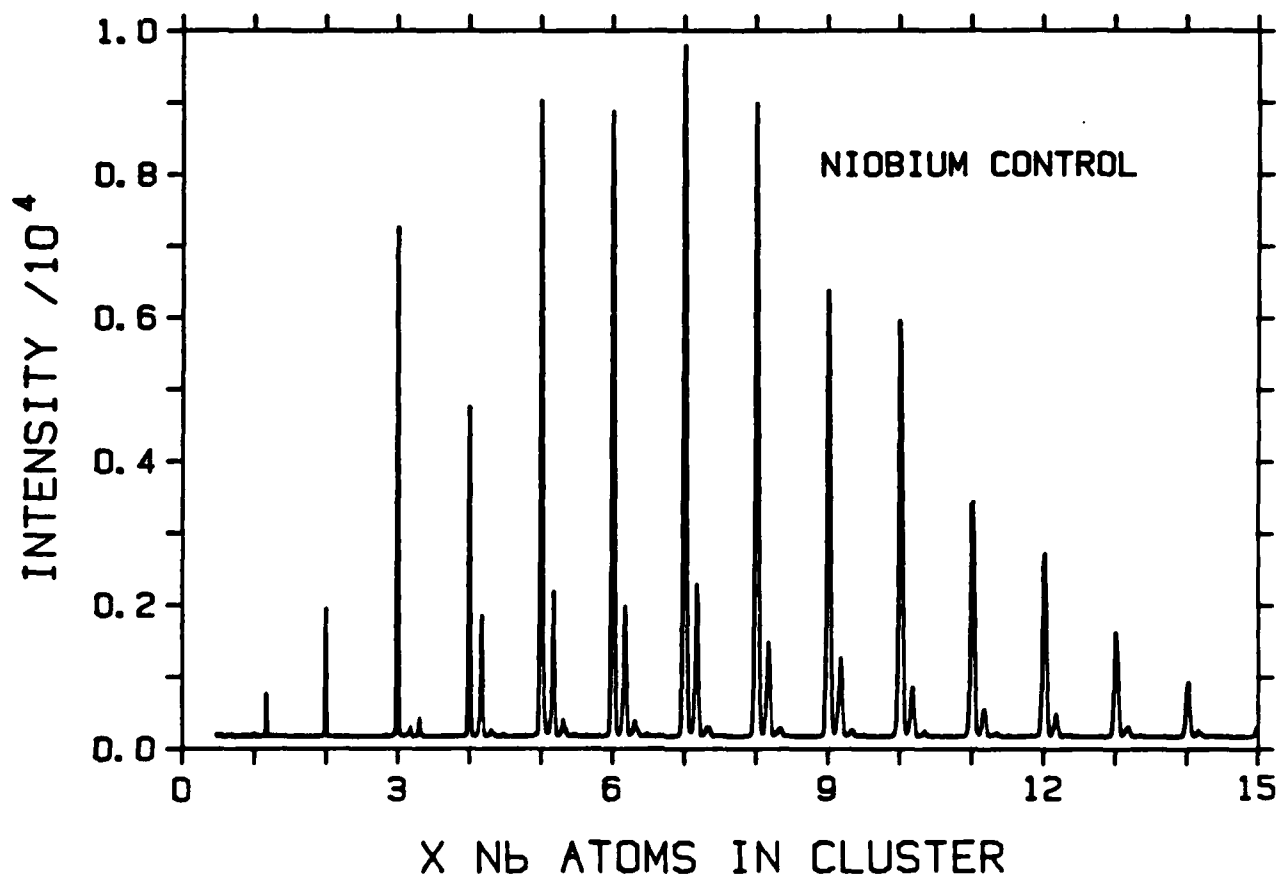
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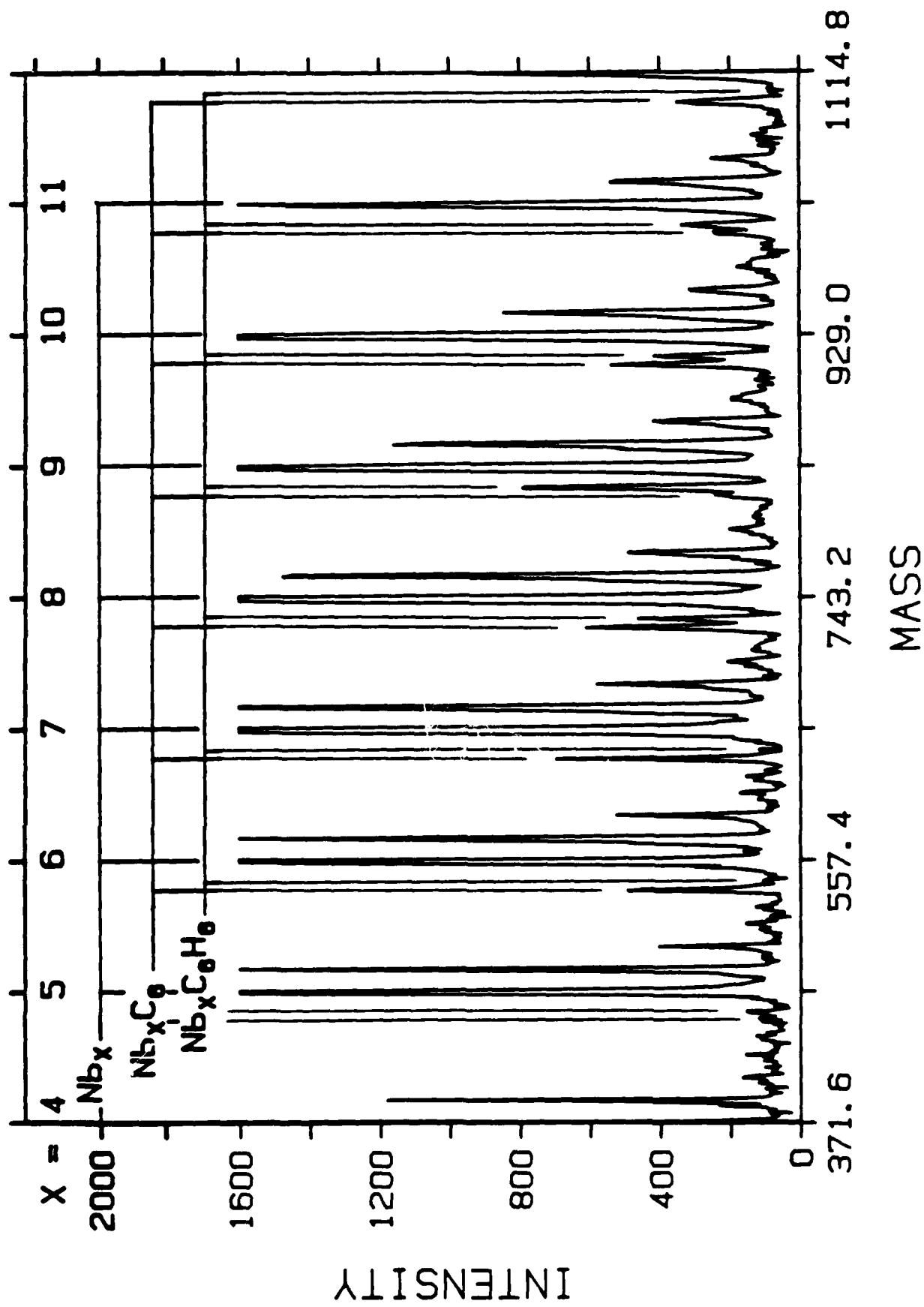
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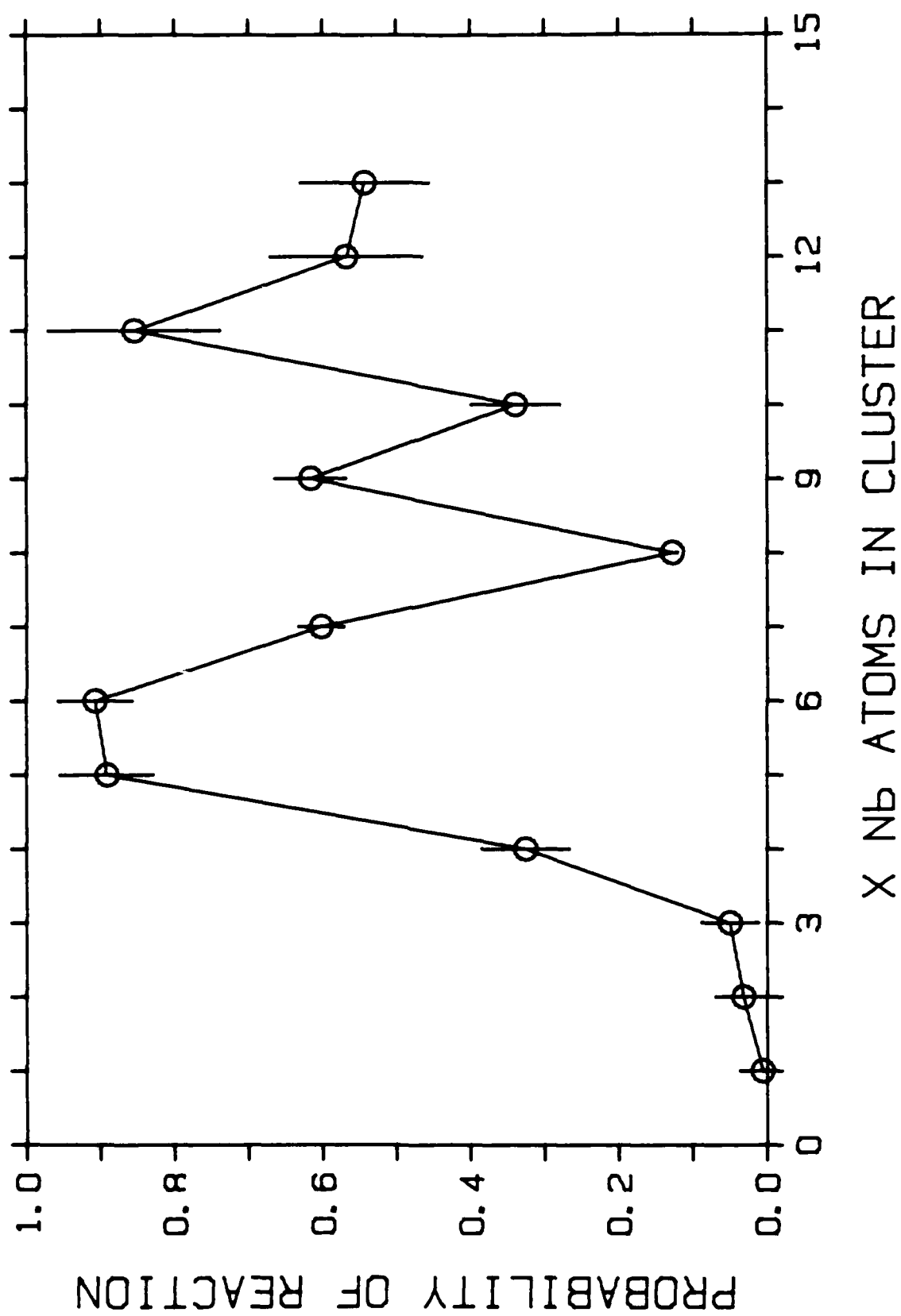
Figure 1. Time-of-flight mass spectra of niobium clusters Nb_x and their reaction products with low pressure benzene vapor in a fast flow reactor. The upper trace (Figure 1a) is the niobium cluster control distribution taken with pure helium in the flow reactor. The lower trace (Figure 1b) is taken under the same conditions as in Figure 1a except that 1.4% benzene vapor was added to the helium reactant gas. The product peaks $Nb_1(C_6H_6)_y$, $Nb_2(C_6H_6)_y$ and $Nb_3(C_6H_6)_y$ are marked for $y = 1-2$.

Figure 2. Expanded portion of Figure 1b showing the dependence of reaction product mass peaks for $Nb_xC_6H_6$ and Nb_xC_6 on the size of the cluster for $x = 4-11$. Labeling of the bare Nb_x niobium clusters as well as the $Nb_xC_6H_6$ and Nb_xC_6 product peaks is included with the number of niobium atoms x indicated.

Figure 3. A plot showing the dependence of the dehydrogenation reaction probability (defined as $I(Nb_xC_6)/\{I(Nb_xC_6H_6)+I(Nb_xC_6)\}$ where I refers to the mass peak intensities) on the number of atoms ($x = 1-15$) in the parent niobium clusters. Error bars represent one standard deviation of the data points taken from five different spectra.







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